(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 921 207 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
09.06.1999 Bulletin 1999/23

(51) Int Cl.6: **C22F 1/18**

(21) Application number: **98309067.1**

(22) Date of filing: **05.11.1998**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **05.11.1997 US 964781**

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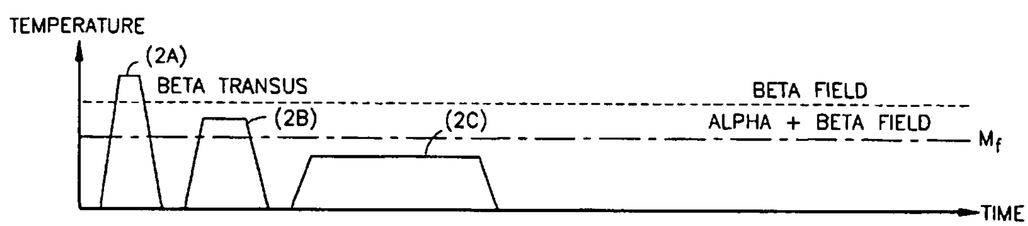
(54) **Method for improving creep properties of titanium alloys**

(57) Processing of alpha plus beta and near-alpha titanium alloys to improve thermomechanical properties including creep resistance and strength that are debited by impurities inherently introduced into the material during alloy production. The process of the invention includes sub-beta forging, above beta transus solutionizing, sub-beta transus solutionizing, and precipitation treating, with cooling subsequent to each solution treatment. Alternatively, the alloy may also be precipitation treated subsequent to the beta solutionizing but before the sub-beta transus solution treatment.

FIG.2



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Description

[0001] This invention relates to the thermo mechanical processing of "alpha plus beta" and "near-alpha" titanium-based alloys for improved creep properties.

[0002] Titanium alloys are widely used in high performance applications because of their relatively low weight and high strength over a wide range of temperatures. Use of these alloys in gas turbine engines, for example, provides significant weight savings over nickel or steel alloys with comparable material characteristics, thereby reducing weight and fuel consumption.

[0003] Alpha plus beta and near-alpha titanium alloys provide both high strength and reasonable formability and are commonly used in the wrought or forged condition.

[0004] Alpha plus beta alloys are those titanium alloys whose low temperature, equilibrium microstructures contain principally alpha and beta phases. Near-alpha alloys are those alpha plus beta alloys that contain primarily alpha phase and a relatively small amount of beta (typically less than about 10% by volume of the beta phase). Alpha plus beta alloys which typically contain about 15-25% by volume of the beta phase are distinguished from beta or near-beta alloys in that they may contain limited amounts of alpha phase.

[0005] Both alpha plus beta and near-alpha alloys may be heat-treated to produce desired properties. In high temperature, static (e.g., non-rotational) gas turbine applications, such as high pressure turbine casings, component life is often limited by the material's creep strength. Thus, these articles are typically processed to optimize creep properties.

[0006] The conventional processing of these materials for high creep strength is as follows. First, the article is forged, usually at a temperature high in the alpha-beta field, that is, at a temperature below that which the material is entirely transformed to the beta phase. This latter temperature is often termed the beta transus. Forging in the beta phase field is also practiced but is less common.

[0007] The forged article is then given a beta solution treatment in which it is heated to a temperature above the beta transus for a period of time and then cooled. Finally, the article is precipitation stabilized at a temperature below the recrystallization temperature. This process is shown schematically in FIG. 1. The resultant microstructure of beta and acicular alpha grains imparts good high temperature creep characteristics.

[0008] Recent industry changes in titanium alloy production processes have resulted in commercial titanium mill stock that contains increased levels of certain impurities such as nickel, iron, and chromium. These impurities impair creep properties. The increased level of impurities may result in manufactured articles that, when processed conventionally, have reduced creep properties and cannot be put into service, must be repaired or replaced on a more frequent maintenance schedule, or must be redesigned to lower the article stress level. Table 1 summarizes creep test results performed on various Ti-6242 forgings that had undergone the conventional heat treatment. The first table entry is for an alloy typical of that resulting from the prior refining techniques, the remaining entries are for actual alloys containing current Ni, Fe and Cr impurity levels. The data demonstrate the general correlation between high levels of impurities and decreased creep life, and also illustrate the substantial reduction in creep properties which results from high levels of Ni, Fe and Cr.

TABLE 1

Impurity Content (ppm)			(hrs) Time to 0.1% Creep Strain at 1025°F/25 ksi (551°C/172. MPa)
Ni	Fe	Cr	
10	350	10	110
55	450	75	38
68	350	85	46
30	280	76	59
98	260	180	2
65	300	71	28.7
77	230	150	27.7
71	210	160	23.6
80	210	170	32.9
150	790	190	13.8
(1) hypothetically alloy representative of prior alloys			
(2) actual alloys			

[0009] While high-purity titanium is commercially available, decreased supply and high demand have resulted in significant cost and procurement time premiums. Therefore, for high temperature applications, it is highly desirable to

be able to use titanium that contains higher levels of impurities than previously thought usable by the industry. Furthermore, it is also desirable to be able to salvage articles that exhibit reduced creep properties.

[0010] In broad terms, the invention provides a method for heat treating a titanium forging, having a characteristic beta transus temperature, and selected from the group consisting of alpha plus beta and near alpha alloys, to improve creep properties comprising the steps of:

a. solution treating the forging above the beta transus;
b. cooling the forging to a temperature below its M_f temperature at a rate that produces acicular alpha;
c. solution treating the forging below but within about 100° F.(55°C) of the beta transus;
d. cooling the forging to a temperature below the M_f temperature at a rate sufficient to produce acicular alpha;
e. precipitation treating the forging at about 800°-1300° F. (426-704°C) for 2-8 hours.

[0011] The invention appears to be especially applicable to alpha + beta and near alpha alloys, especially of Ti-6242, which contain more than about 20 ppm Ni, more than about 30 ppm Cr, and more than about 60 ppm (Ni + Cr). The invention process will be particularly useful in processing alloys containing more than about 25 ppm Ni, more than about 50 ppm Cr and more than about 85 ppm (Ni + Cr). Since the Ni, Fe and Cr impurities are present in the starting titanium basis material, similar impurity levels will be found in other titanium alloys such as those described in Table 2. Based on the similarity of the metallurgical phenomena in Ti-6242 and the other Table 2 alloys, similar benefits are anticipated for all Table 2 alloys.

[0012] Thus the present invention produces articles, formed from alpha plus beta or near-alpha titanium alloys containing relatively high levels of impurities, that exhibit improved creep properties (relative to the same compositions conventionally processed), by forging the starting material, usually but not essentially in the alpha plus beta field below the beta transus, solution treating the forged article at a temperature above the beta transus, cooling the article, solution treating the article at a temperature below the beta transus, cooling the article again, and precipitation treating. An additional precipitation treatment may be performed prior to the sub-beta solution treatment.

[0013] The invention allows the use of alloys containing amounts of transition metal impurities that exhibit debited creep properties compared to purer alloys which were common in the past. The invention also improves articles that could not otherwise be utilized because they exhibit creep properties below a minimum requirement.

[0014] The global supply of purer titanium alloys is and is anticipated to remain limited, resulting in higher material prices and longer procurement periods. By allowing use of more readily available, lower-priced, higher impurity alloys, the invention decreases delivery times and end-user costs.

[0015] Some preferred embodiments of the present invention will now be described, by way of example only, with reference to the accompanying drawings in which:

FIG. 1 is a graphical representation of the prior art post forging heat treatment.
FIG. 2 is a graphical representation of a post-forging heat treatment of the present invention.
FIG. 3 is a graphical representation of an alternate post-forging heat treatment of the present invention.

[0016] Recent industry changes in the processing of titanium ores have resulted in titanium materials that contain higher amounts of impurities. Impurities such as nickel and iron are known to reduce creep properties. The inventor has discovered that the higher levels of chromium now present in contemporary materials, in conjunction with higher levels of nickel and iron, may impair creep properties to the degree that such titanium alloys (with greater impurity contents than in the past) long-used for particular purposes, such as gas turbine components, are no longer suitable because of reduced creep properties. The impaired creep properties of these high impurity alloys are believed to be an unanticipated effect of the current mill production techniques. Titanium alloys produced using the older, now-obsolescent processes typically contained about 10 ppm of nickel, about 350 ppm of iron and about 10 ppm of chromium; current materials often contain impurities exceeding those levels, in many instances by a substantial amount.

[0017] The present invention substantially improves the creep properties of forged articles produced from such high impurity near-alpha or alpha plus beta titanium alloys by way of thermal processing. A preferred processing method of the invention comprises the following steps.

[0018] First, an alpha plus beta or near alpha alloy material is forged to a desired configuration. Preferably forging is performed below the beta transus temperature to ensure that excessive grain growth does not occur, but forging as much as 200°F (111°C) above the beta transus is possible. The forging temperature depends upon the nature of the article. A sub-beta forged alpha plus beta or near-alpha articles is typically formed high in the alpha plus beta field, below, but within about 200°F (111°C) of its beta transus to ensure sufficient plasticity. Thin sections, typically less than about .5 in (13 mm) can be air cooled while thick sections, typically greater than about 2 inches (50 mm) are typically liquid quenched. The invention may also be defined as the heat treatment portion of the process as applied to previously forged alloys.

[0019] Second, as shown in FIG. 2, step 2A, the forged article is solution treated above the beta transus. Temperatures of 25°-100°F (14-55°C) above the beta transus are preferable, with about 50°F (28°C) being preferred, for about one-half to two hours. The article is then cooled to a temperature below the martensite finish temperature (M_f). The cooling rate is important.

[0020] The article must be cooled at a rate fast enough to produce acicular alpha, as opposed to the equiaxed alpha grains that form upon slow cooling, but slow enough to avoid excessive production of martensite. Martensite in excess of about 5 vol % is considered excessive. Too high a cooling rate can also result in high residual stresses and warping. Those skilled in the art will be able to effect a cooling rate that produces the above desired result, as they understand that the actual cooling rate required depends upon the material's time-temperature-transformation characteristics, the temperature from which cooling occurs and the size (thickness) of the alloy article. Typically, however, actual metal cooling rates of from about 150 to about 450°F/min (83-250°C/min) are desired and preferably about 200-400°F/min (111-222°C). Applied to thinner section alpha plus beta and near-alpha titanium alloys, the desired cooling rate might be achieved by air cooling. Thicker section material may require fan air cooling, oil quenching or water quenching to achieve the proper cooling rate.

[0021] The article is then sub-beta solution treated as shown in FIG. 2, step 2B, at a temperature below but within about 100°F (55°C) of the beta transus. Treatment times of about one-half to four hours are preferred. The article is then cooled to below M_f at a rate that produces acicular alpha as discussed above.

[0022] Finally, the article is precipitation stabilized as shown in FIG. 2, step 2C. Alpha plus beta and near-alpha alloys typically exhibit precipitation at temperatures of about 800°-1300°F (427-704°C). The industry practice is to precipitation treat at a temperature above the operating temperature of the material for approximately 2-8 hours to optimize material properties and minimize microstructural and dimensional changes during service.

[0023] In addition, as shown in FIG. 3, a precipitation cycle, step 3B, may be performed after the beta solution treatment, step 3A, but before the sub-beta solution treatment, step 3C, followed by precipitation step 3D. The practical effect of this is that the invention may be applied to an article that has undergone the prior art heat treatment. The invention may thus be used to salvage such processed articles that are found, to possess unacceptable creep properties.

[0024] The invention produces a microstructure of acicular alpha within a beta phase matrix in $\alpha + \beta$ alloys including those classified as near alpha alloys and especially those referred to as 6242 alloys. The sub-beta solution treatment high in the alpha plus beta field produces aciculae of much greater thickness than the prior art heat treatment, shown in FIG 1 to consist of a relatively short beta treatment, step 1A, followed by a much longer precipitation cycle, step 1B. As the high creep strength is believed to result primarily from the acicular alpha phase, the invention may be applied to alpha plus beta alloys containing up to about 25% beta phase. In near-alpha alloys, where the beta phase may present in an amount of less than about 5% by volume, the beta grains would be located along the alpha grain boundaries.

[0025] As noted above, the invention may be applied to alpha plus beta alloys, including near-alpha alloys. Table 2 lists some, but not all, alloys for which the invention is useful. Those familiar with the art will be able to determine other alloys for which the invention would be useful.

TABLE 2

		Nominal Composition, wt. %						
	Alloy	Al	Sn	Zr	Mo	V	Nb	Other
Near Alpha	Ti-811	8.0	-	-	1.0	1.0	-	-
	Ti-6242	6.0	2.0	4.0	2.0	-	-	0.08 Si
	IMI 829	5.8	4.0	3.5	0.5	-	0.7	0.35 Si, 0.06 C
	IMI 834	5.5	3.5	3.0	0.25	-	1.0	0.3 Si
Alpha Beta Alloys	Ti-6A1-4V	6.0	-	-	-	4.0	-	-
	Ti-7A1-4Mo	7.0	-	-	4.0	-	-	-
	Ti-6246	6.0	2.0	4.0	6.0	-	-	-
	Ti-17	5.0	2.0	2.0	4.0	-	-	4.0 Cr

EXAMPLE

[0026] A thin-section article may be forged from Ti-6242. Ti-6242 is considered a near-alpha alloy and has a allowable composition of 5.5%-6.5% Al, 1.8%-2.2% Sn, 3.6%-4.4% Zr, 1.8%-2.2% Mo, 0.06 - 0.10 % Si and small amounts of

other (impurity) elements. This composition gives Ti-6242 a beta transus of about 1825°F (996°C), and forging in a temperature range of about 1700°-1800°F (927°-982°C) provides sufficient plasticity to forge a thin-section article. The forged article would then be heated and held at a temperature of about 50°F (28°C) above the beta transus, in this case at about 1875°F (1025°C), for 0.5-2 hours, followed by air cooling to below the Ti-6242 martensite finish temperature of 1425°F (774°C). It would not be necessary, although not objectionable, to cool the article to ambient temperature. The article would then be heated and held at a temperature between about 1725°F (940°C) and about 1800°F (982°C) for about 0.5-4 hours, and again cooled to below about 1425°F (774°C). Lastly, the article would be precipitation stabilized for about 2-8 hours at a temperature above its maximum service temperature. As the practical use temperature limit of Ti-6242 is about 1050°F (565°C), the article may be stabilized at about 1100°F (593°C).

[0027] The invention was applied to six samples of high impurity Ti-6242 forgings. The design requirement for these articles specified a minimum of 20 hours to 0.1% creep strain under test conditions specified in Table 3. As Table 3 shows, the invention significantly improved the creep properties of those articles that originally exhibited poor creep characteristics after the prior heat treatment, elevating creep strength to serviceable levels. Therefore, the invention may be applied to articles that possess poor creep properties due to high impurity levels. The present invention thus allows the use of more readily available and less expensive high-impurity titanium in high temperature applications. Samples 1 and 6 show the invention benefits. Samples 3 and 5 show an anomalous result, a reduction in creep life. It appears that samples having relatively high creep lives, seem to potentially undergo a reduction in creep life when treated by the invention. Applicant applies this invention process to high value forgings and tests a coupon at least one forging from each heat of titanium alloy, where each heat of alloy has a specific chemistry. Applicants' preferred process is to process all forgings from a single alloy heat conventionally, test for creep life and then apply this process as a restorative process to forgings which exhibit creep lives below 20 hours.

TABLE 3

	Impurity Content (ppm)			Time to 0.1% Creep Strain at 1025°F/25 ksi (hrs) (551°C/172.6 MPa)	
Sample No.	Ni	Fe	Cr	Prior Art Heat Treatment	Present Invention Heat Treatment
1	98	260	180	2	22
2	65	300	71	28.7	29.0
3	77	230	150	27.7	20.9
4	71	210	160	23.6	35.3
5	80	210	170	32.9	12.3
6	150	790	190	13.8	24.2

Claims

1. A method for heat treating a titanium forging, having a characteristic beta transus temperature, and selected from the group consisting of alpha plus beta and near alpha alloys, to improve creep properties comprising the steps of:

   a. solution treating the forging above the beta transus;
   b. cooling the forging to a temperature below its M_f temperature at a rate that produces acicular alpha;
   c. solution treating the forging below but within about 100°F.(55°C) of the beta transus;
   d. cooling the forging to a temperature below the M_f temperature at a rate sufficient to produce acicular alpha;
   e. precipitation treating the forging at about 800°-1300° F. (426-704°C) for 2-8 hours.

2. A method as claimed in claim 1 wherein the forging contains more than about 60 ppm (Ni + Cr).

3. A method as claimed in claim 1 or 2 wherein the solution treatment above the beta transus is performed about 25-100° F. (14-55°C) above the beta transus.

4. A method as claimed in claim 1, 2 or 3 wherein the solution treatment above the beta transus is performed for about 0.5-2 hours.

5. A method as claimed in any preceding claim wherein the sub-beta solution treatment is performed for about 0.5-4 hours.

6. A method as claimed in any preceding claim wherein the precipitation treatment is performed at about 1100° F.

7. A method as claimed in any preceding claim wherein the titanium alloy consists of Ti-6242.

8. A method as claimed in claim 7 wherein the alloy is forged at a temperature of about 1700°-1800°F (927-982°C).

9. A method as claimed in claim 7 or 8 wherein the beta solution treatment is performed at about 1875° F (1624°C).

10. A method as claimed in claim 7, 8 or 9 wherein the sub-beta solution treatment is performed at 1725°-1800°F (940-982°C).

11. A method as claimed in claims 7 to 10 wherein the forged alloy is cooled to below 1425°F (774°C) subsequent to the beta and sub-beta solution treatments.

12. A method as claimed in any preceding claim further comprising, after the step of cooling the forging to a temperature below its M_f temperature at a rate sufficient to produce acicular alpha; the addition step of precipitation treating the forging at about 800°-1300° F. (426-704°C) for 2-8 hours.

13. A method as claimed in any preceding claim wherein the method is applied as a restorative process to forgings which have already undergone heat treatment.

14. An alpha plus beta or near alpha titanium alloy article produced according to the method of any preceding claim.

FIG.1
PRIOR ART

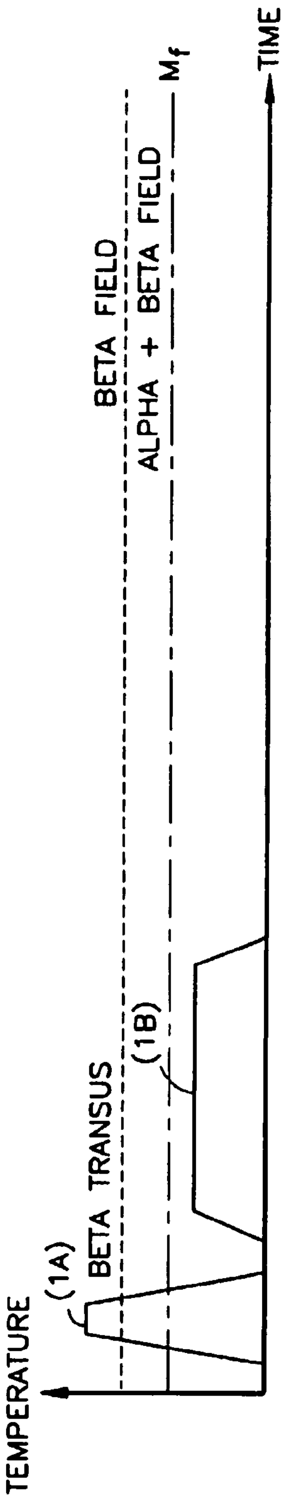


FIG.2

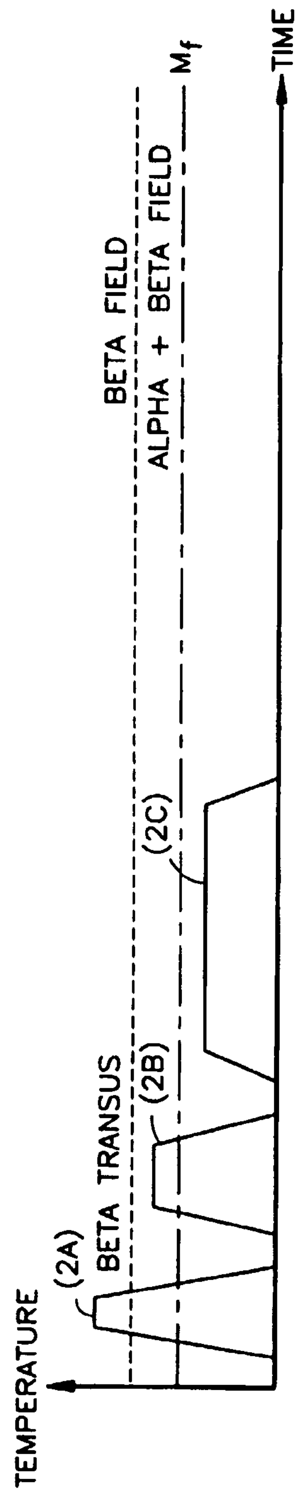
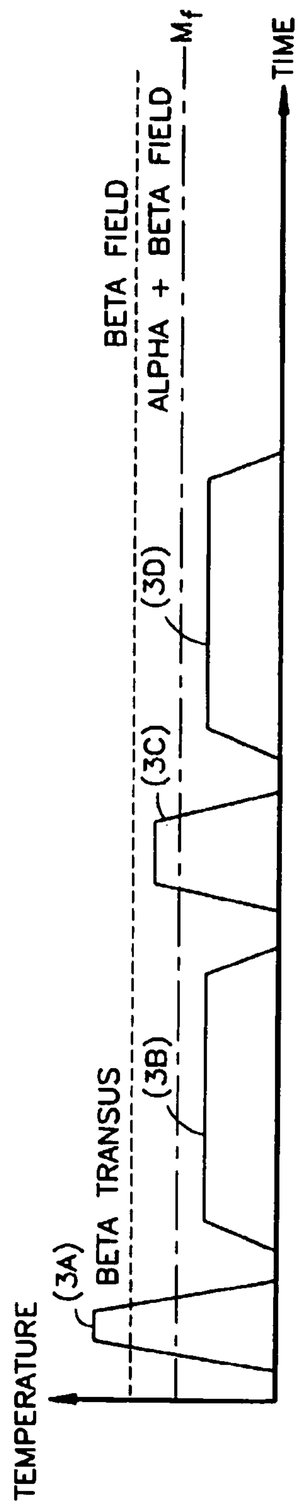


FIG.3



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EUROPEAN SEARCH REPORT

Application Number
EP 98 30 9067

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	WO 93 22468 A (ALUMINUM CO OF AMERICA ;CHAKRABARTI AMIYA K (US); KUHLMAN GEORGE W) 11 November 1993 * page 5, line 27 - page 6, line 13; claims 1,3-6 *	1-14	C22F1/18
A	EP 0 181 713 A (GARRETT CORP) 21 May 1986 * claims 1-7 *	1	
A	US 3 901 743 A (SPRAGUE ROBERT A ET AL) 26 August 1975 * column 2, line 37 - line 39 * * column 4, paragraph 2; claim 1 *	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C22F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24 February 1999	Gregg, N

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24-02-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9322468 A	11-11-1993	US 5399212 A	21-03-1995
		EP 0672195 A	20-09-1995
EP 0181713 A	21-05-1986	US 4631092 A	23-12-1986
		CA 1244327 A	08-11-1988
		JP 1036551 B	01-08-1989
		JP 1554641 C	23-04-1990
		JP 61106739 A	24-05-1986
US 3901743 A	26-08-1975	DE 2255313 A	24-05-1973
		FR 2162856 A	20-07-1973
		JP 48059014 A	18-08-1973

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